LIQUEFACTION OF COAL IMPREGNATED WITH CATALYST DURING PRESWELLING

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ABSTRACT

The effect of impregnating coal with slurry phase catalysts during solvent preswelling on coal conversion was investigated. Black Thunder subbituminous coal which was either untreated or pretreated with aqueous SO_2 was used. The coal was placed into the swelling solvents, THF, methanol or isopropanol, for 96 hr prior to liquefaction. Slurry phase catalysts, Mo naphthenate, Molyvan L and Ni octoate, were introduced into the swelling solvents; catalyst uptake by coal was 90 to 95% of the catalyst introduced. Coal conversions of these impregnated coals were obtained at 410 °C in reaction solvents of 1-methylnaphthalene, coal-derived V1074, and dihydroanthracene, and were compared to those obtained with swelled and nonswelled coals. The swelling solvent and the SO_2 pretreatment affected the amount of coal conversion obtained. Coal conversions achieved with impregnated coals were somewhat less than those achieved when the catalyst was added directly to the reactor.

INTRODUCTION

Increases in the liquefaction conversion and production of upgraded product from subbituminous coal are desirable to make the process a feasible option for production of transportation of fuels. To this end, a process was conceptualized and tested. The conceptual process involves several steps: (1) coal is pretreated with aqueous SO_2; (2) the pretreated coal is then swelled in a hydrogen bonding solvent in which is placed a slurry phase catalyst; (3) during swelling the slurry phase catalyst is deposited within the pores of the coal; and (4) the impregnated coal is liquefied having the catalyst in intimate contact with the reacting coal molecules.

The research described herein tested the conceptual process using both untreated and SO_2 treated coal. The reason that a substantial number of experiments was performed with the untreated coal was that previous results[1] indicated that swelling coal prior to liquefaction was more beneficial to coal conversions of untreated coal than of SO_2 treated coal. Reactions were performed (1) without swelling prior to liquefaction; (2) with swelling prior to liquefaction with the catalyst being added directly to the reactor; and (3) with swelling prior to liquefaction with catalyst being added to the swelling solvent. Three different swelling solvents, tetrahydrofuran (THF), isopropanol, and methanol, were used[2]; three different catalysts, Mo naphthenate, Molyvan L and Ni octoate, were used; and three different reaction solvents, 1-methylnaphthalene, a relatively inert solvent; V1074, a coal-derived solvent and dihydroanthracene, a hydrogen donor solvent, were also used.

EXPERIMENTAL

Materials. Liquefaction reactions were performed using untreated and aqueous SO_2 treated Black Thunder coals. The swelling solvents, THF, methanol, and isopropanol were obtained from Fisher and were used as received. The liquefaction reaction solvents used were 1-methylnaphthalene (1-MN) (98% purity) and 9,10-dihydroanthracene (DHA), which were obtained from Aldrich, and V1074, a coal-derived solvent, supplied by Amoco. The catalysts used were Molyvan L from Vanderbilt Chemical and Mo naphthenate and Ni octoate from Shepherd Chemical Company; and Ni naphthenate from Strem Chemical Company.

Swelling and Reaction Procedures. Untreated and SO_2 treated Black Thunder coals were swelled by introducing 1.33 g maf coal to the swelling tube and then adding 7 ml of solvent. Molyvan L, Mo naphthenate, and Ni octoate catalysts were charged to the swelling solvent at 1.05 times 600 to 800 ppm of active metal, the amount used when the catalyst was added directly to the liquefaction reactions. The coal was then allowed to sit unagitated in the swelling solvent for 96 hr. These experiments were designated with a "N" on the tables. Several experiments, designated with an "A" on the tables, were performed in which the coal and swelling solvent were agitated using an orbital shaken at 250 rpm during the 96 hr swelling period. Molyvan L was also added to the swelling solvent at twice the loading typically used, 1400 to 1600 ppm of active metal. These experiments in which the catalyst level was doubled are designated with a "D" on the tables.

Liquefaction reactions using untreated Black Thunder coal in 1-MN were performed at 410°C for both 20 and 30 min in stainless steel tubular microreactors. The liquefaction reactions for SO_2 treated Black Thunder coal in 1-MN and for untreated Black Thunder coal in V1074 and DHA were conducted for 30 min. Each reaction contained ~1.33 g of maf coal, 2 g of solvent, 0.67 g of pyrene (PYR) and residual swelling solvent that remained in the swelled coal. The amount of solvent absorbed in the coal after swelling differed for each swelling solvent. The amount of solvent retained in the coal ranged from 0.6 to 1.0 times the coal mass. The amount of catalyst taken up by coal was obtained for selected reactions using x-ray fluorescence spectroscopy. Hydrogen gas was introduced at 1250 psig at ambient temperature. The reactor was well-agitated at 450 cpm.

Analysis. Products from the liquefaction reactions were removed from the reactor with THF. The conversion of the coal to THF solubles was determined. For the reactions where analysis of catalyst uptake was obtained, the values for the catalyst loading are given, otherwise, the presumed amount deposited ranged from 90 to 95% of the 600 to 800 ppm of active metal loaded on a per gram of coal basis. The amount of PYR hydrogenation to hydrogenated products was obtained by gas chromatographic analyses using a Varian Model 3400, a J&W DB-5 fused silica capillary column and flame ionization detection. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from PYR as a percentage of the moles of hydrogen required to form the most hydrogenated product, perhydropyrene. The hydrogenation products obtained from PYR were dihydropyrene (DHP) tetrahydropyrene (THF) and hexahydropyrene (HHP).

RESULTS AND DISCUSSION

In the liquefaction reactions performed in this research, two primary parameters were measured to evaluate the efficacy of the catalyst impregnation step. The first parameter was the conversion of Black Thunder coal to THF soluble material. The second parameter measured was the hydrogenation reactivity of the added aromatic, PYR, in the system. By determining the conversion of PYR to hydrogenated species and the percent hydrogenation to partially saturated products, the intrinsic activity of the catalyst added to the reaction system in a particular manner could be obtained. The only products observed from PYR were DHP, THP, and HHP. Usually, higher conversions resulted in the production of all three products. However, DHP was the primary hydrogenation product produced in all reactions. Both THP and HHP, when formed, were always minor products.

Reactions in 1-Methylnaphthalene. Liquefaction reactions performed in the nondonor solvent 1-MN using untreated and SO_2 treated Black Thunder coal are presented in Tables 1 and 2, respectively. Evaluation of the coal conversions obtained with the untreated (Table 1) or SO_2 treated coal (Table 2) indicated that the presence of a Mo or Ni based catalyst regardless of method of introduction increased coal conversion. The Molyvan L catalyst was more active for both coal conversion and PYR hydrogenation than was either Ni octoate or Mo naphthenate reacted without sulfur. Longer reaction times of 30 min resulted in higher coal and PYR conversions than did shorter reaction times of 20 min. The type of swelling solvent used made a difference in coal conversion, depending on the solvent used. Methanol appeared to be the most effective swelling solvent for Molyvan L while isopropanol was most effective for Ni octoate. Agitation of the swelling solvent with coal and catalyst present did not increase coal conversion. Doubling the catalyst loading and the amount impregnated into the coal yielded only a slight improvement in coal conversion but a more substantial improvement in PYR conversion. When the coal conversion of coal impregnated with catalyst during the swelling process was compared to that achieved when the catalyst was added directly to the reactor, the Molyvan L systems with THF and isopropanol swelling solvents yielded less conversion with impregnated catalyst while the systems with methanol yielded more. For Ni octoate, all of the impregnated coals yielded less conversion than the coal reacted with the catalyst in the slurry phase. Pyrene conversions were also higher when the catalyst was added directly to the reactor.

Reactions with SO_2 treated coal showed that swelling of the pretreated coal had less effect than swelling the untreated coal. Impregnation of Molyvan L with any of the three swelling solvents resulted in approximately 5% less coal conversion. Pyrene conversion remained high with Molyvan L; in some reactions adding the catalyst directly to the reactor yielded more activity while in other reactions the impregnated catalyst was more active. The type of swelling solvent had a stronger influence on coal conversion when Ni octoate was used as a catalyst. Higher coal and PYR conversions were achieved with Ni octoate when methanol was used as a swelling solvent than when either THF or isopropanol was used.

Reactions in V1074. A series of reactions was performed using THF as the swelling solvent and coal-derived V1074 as the reaction solvent (Table 3). Comparison of the reaction solvent V1074 to 1-MN for liquefaction of untreated Black Thunder coal showed a higher coal conversion with Molyvan L when no swelling prior to liquefaction was used. This advantage

of the coal-derived solvent was maintained when the coal was swelled prior to reaction and reacted without catalyst. However, when coal was swelled prior to liquefaction and Molyvan L was added either directly to the reactor or to the swelling solvent, the reaction solvent 1-MN yielded slightly higher coal conversion and nearly equivalent pyrene conversions. The coal and pyrene conversions were quite similar with Ni octoate in the two reaction solvents. With V1074, the highest coal conversion achieved occurred without prior swelling, followed by swelling with THF and adding the catalyst to the reactor; the least coal conversion was achieved when either catalyst was added to the THF swelling solvent. Substantial variability in coal and pyrene conversion occurred when Molyvan L was introduced into the swelling solvent indicating nonuniform absorption of the catalyst by the coal.

Reactions in Dihydroanthracene. Higher conversions of Black Thunder coal occurred in DHA when no catalyst was used. The hydrogen donor solvent promoted noncatalytic conversion of Black Thunder coal yielding 82.4% coal conversion after swelling in THF while 72.0% was achieved in V1074 and 59.7% in DHA. The highest coal conversion with Molyvan L in DHA was achieved without prior swelling, intermediate coal conversion occurred with swelling in THF and catalyst added directly to the reactor, while the lowest coal conversion occurred when the catalyst was added to the swelling solvent. The difference between the high and low values, though, was only 5%.

SUMMARY

The improvement in coal conversion expected by impregnating coal during the swelling process was not achieved. Swelling of untreated Black Thunder coal made the coal more accessible and more reactive under liquefaction conditions. However, absorbing the catalyst into coal, prior to liquefaction, thereby, making the catalyst more accessible to the dissolving coal molecule, did not achieve increased coal conversion at the liquefaction conditions used.

REFERENCES

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Table 1. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None				
None	0	NA[a]	NA	49.3±0.8	3.5±1.1	2.1±0.6
Molyvan L	709±39	NA	NA	82.4±3.0	30.0±5.4	11.2±2.4
Ni Octoate	604± 6	NA	NA	70.7±4.1	6.8±0.3	2.3±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	34.2±7.0	59.7±8.9	0.0	0.0
Molyvan L	661±33	N	37.8±1.9	87.3±1.6	18.6±1.3	6.2±0.4
Ni Octoate	615± 6	N	41.3±0.6	77.0±0.1	2.4±0.1	1.2±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Mo Naphthenate	683	A	35.0±4.5	18.6±1.3	3.5±0.2	1.8±0.4
Molyvan L	544	N	40.4±1.8	81.9±1.6	15.1±1.8	5.7±0.4
Molyvan L	NM[c]	A	52.3±3.2	73.6±3.0	14.7±5.0	5.7±1.9
Molyvan L	1143	D	41.0±2.7	84.8±1.1	28.6±2.5	11.0±1.2
Ni Octoate	569	N	38.9±5.	74.8±12.9	11.1±11.0	4.7±4.1
Reaction Time: 20 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Mo Naphthenate	608±9.2	A	37.1±12.0	53.1±3.3	2.6±0.5	1.7±0.2
Molyvan L	NM	N	38.7±3.2	67.5±5.4	4.8±3.5	2.1±1.3
Ni Octoate	599	N	34.1±3.3	60.8±3.2	2.4±0.3	1.3±0.1

Table 1 (Continued)

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Reactor		
None	0	N	26.7±0.8	53.9±2.8	1.0±0.3	0.8±0.2
Molyvan L	690±19	N	18.6±0.6	88.0±0.9	24.3±1.8	8.5±1.1
Ni Octoate	698±70	N	18.6±0.6	85.5±0.1	10.9±0.4	4.0±0.4
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	644	N	25.2±4.9	68.4±0.0	3.0±0.8	1.7±0.5
Molyvan L	1261	D	26.2±3.4	88.8±0.5	25.7±2.7	9.9±1.3
Ni Octoate	653	N	23.3±0.8	70.1±1.1	3.5±0.4	1.9±0.1
Reaction Time: 20 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	637	N	25.4±9.1	67.6±0.1	2.8±0.8	1.9±0.1
Ni Octoate	613±6.4	N	20.6±4.5	64.4±0.4	2.3±0.4	1.4±0.3
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Reactor		
None	0	N	16.9±5.5	61.7±1.1	0.8±1.1	0.6±0.8
Molyvan L	623±37	N	17.9±6.9	88.1±0.4	18.7±0.8	6.6±0.3
Ni Octoate	658±1.4	N	16.3±3.8	77.6±1.1	2.2±0.4	1.1±0.1
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to the Swelling Solvent		
Molyvan L	645±26	N	18.2±1.1	79.9±0.8	16.9±2.3	6.5±0.8
Molyvan L	NM	D	22.8±1.5	81.9±1.8	28.2±0.4	10.9±0.3
Ni Octoate	667±70	N	15.6±3.7	75.2±0.8	3.9±0.6	1.9±0.3
Reaction Time: 20 min		Swelling Solvent: Isopropanol		Catalyst Added to the Swelling Solvent		
Molyvan L	572	N	18.6±0.6	68.2±4.0	4.5±1.8	1.9±0.7
Ni Octoate	699	N	15.6±3.7	64.8±3.7	4.3±0.4	2.2±0.1

[a]A = agitated: samples were agitated with catalyst for 96 hr; N = not agitated for 96 hr swelling period; D = catalyst level doubled. [b]NA = not applicable. [c]NM = not measured; catalyst loading should be between 550 and 750 ppm.

Table 2. Coal and Pyrene Conversions for SO_2Treated Black Thunder Coal Reacted in 1-Methylnaphthalene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None				
None	0	NA[a]	NA	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	623±12	NA	NA	88.5±0.7	27.8±3.0	10.4±0.6
Ni Octoate	696±143	NA	NA	76.3±4.2	12.5±3.5	4.2±1.2
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	87.6±2.7	58.0±9.5	0.0±0.0	0.0±0.0
Molyvan L	683±53	NA	79.5±0.8	91.2±1.5	25.4±0.1	9.1±0.1
Ni Octoate	665±23	N	97.4±3.7	72.5±5.8	2.2±0.4	1.2±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	638	N	76.1±18.2	86.0±2.2	31.4±0.8	12.5±0.4
Ni Octoate	659	N	58.9±26.7	71.4±4.1	6.9±1.2	3.1±0.4
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Reactor		
None	0	N	38.4±2.3	41.8±2.4	1.5±0.1	1.0±0.0

Table 2. (Continued)

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Molyvan L	672±18	N	36.9±7.4	90.0±1.3	30.0±4.4	11.2±1.5
Ni Octoate	655±2.1	N	31.6±7.4	78.7±1.1	4.9±0.8	1.8±0.6
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	NM[c]	N	43.7±5.2	85.1±5.7	26.8±2.8	11.1±1.6
Ni Octoate	NM	N	33.4±4.8	78.4±0.2	7.1±0.5	3.1±0.1
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Reactor		
None	0	N	45.0±0.0	56.4±3.0	1.6±0.1	1.1±0.1
Molyvan L	642±25	N	38.6±5.0	91.3±0.6	21.3±2.4	8.0±1.1
Ni Octoate	674±26	N	32.3±6.4	73.9±5.1	3.9±0.6	2.1±0.0
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Swelling Solvent		
Molyvan L	NM	N	32.5±1.2	87.6±1.0	26.0±0.2	10.4±0.1
Ni Octoate	NM	N	25.0±0.0	67.9±2.3	5.0±0.2	2.4±0.0

[a]NA = not applicable. [b]N = not agitated during 96 hrs swelling period. [c]NM = not measured.

Table 3. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in V1074

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation %
Reaction Time: 30 min		Swelling Solvent: None		Catalyst Added to Reactor		
Molyvan L	652±18	NA[a]	NA	84.7±1.0	14.9±2.8	5.7±1.1
Ni Octoate	668±41	NA	NA	79.8±3.5	5.5±4.4	2.0±1.6
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	25.0±3.3	72.0±1.7	5.3±0.1	3.0±0.1
Molyvan L	670±57	N	38.7±9.7	82.8±2.0	28.0±0.3	11.8±0.3
Ni Octoate	663±4.2	N	35.0±4.5	77.2±1.8	6.4±0.0	3.3±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	NM[c]	N	38.3±1.1	76.0±8.1	14.1±2.3	6.1±0.8
Ni Octoate	NM	N	26.7±0.8	79.5±3.5	4.6±1.5	2.5±0.7

[a]NA = not applicable. [b]N = not agitated for 96 hr swelling period. [c]NM = not measured; catalyst loading should be between 500 and 700 ppm.

Table 4. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in Dihydroanthracene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (mol %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None		Catalyst Added to Reactor		
Molyvan L	677±23	NA[a]	NA	89.7±0.2	15.2±4.5	5.4±1.8
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	36.5±2.3	82.4±2.1	9.3±0.2	6.0±0.1
Molyvan L	658±33	N	22.2±0.7	87.3±2.8	23.5±4.7	9.4±1.8
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	NM[c]	N	41.0±6.4	84.5±0.4	8.9±2.3	4.6±0.8

[a]NA = not applicable. [b]N = not agitated for 96 hr swelling period. [c]NM = not measured; catalyst loading should be between 500 and 700 ppm.